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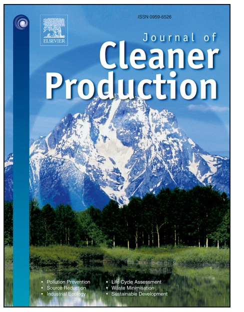

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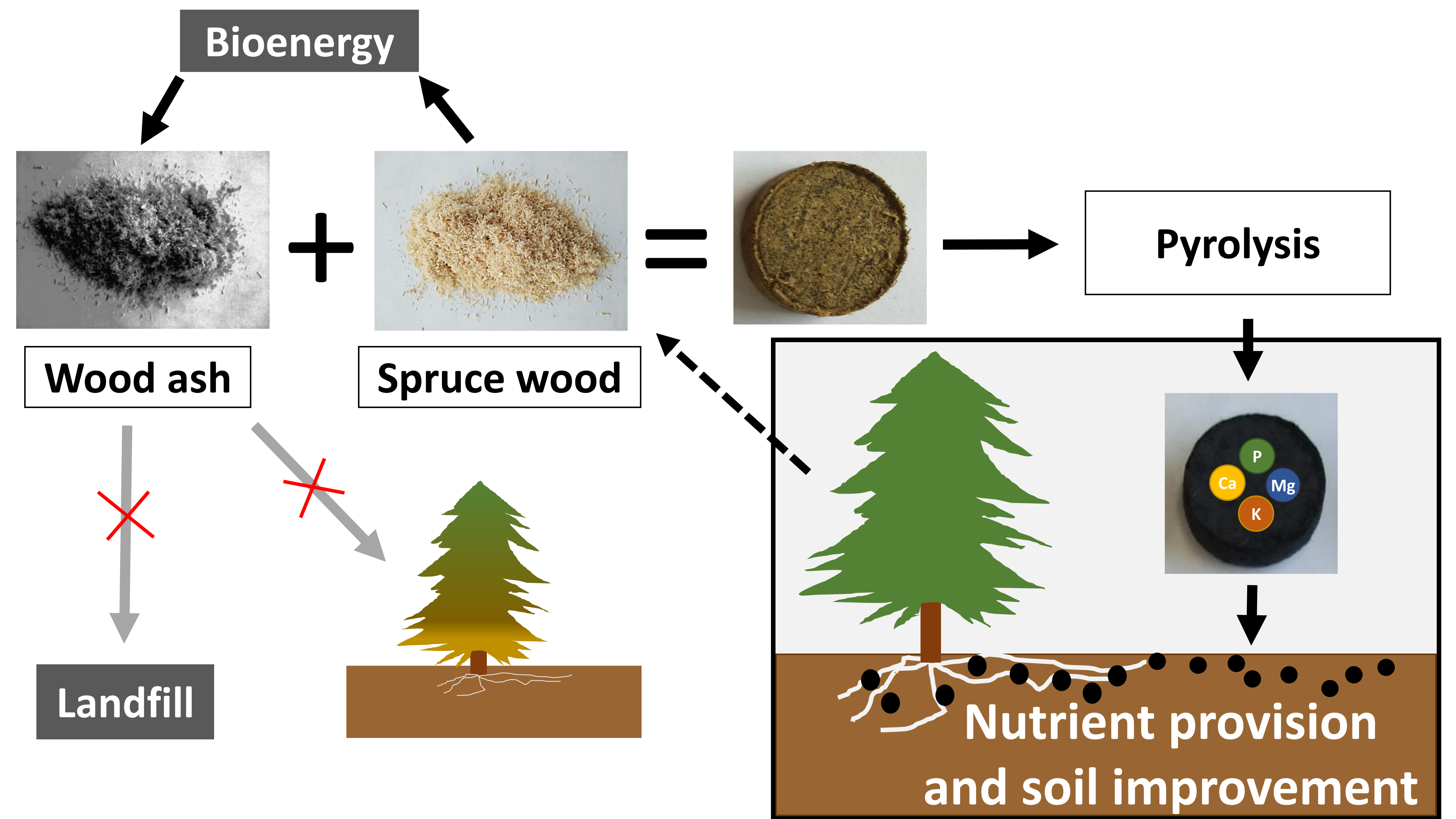
Bioenergy
Wood ash
Spruce wood
Pyrolysis
Landfill
P
Ca
Mg
K
Nutrient provision
and soil improvement

Unexplored potential of novel biochar-ash composites for use as organo-mineral fertilizers

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Abstract

Application of wood ash on forest and agricultural soils can provide nutrients and increase soil pH, however, it changes the soil chemistry rapidly and temporarily, often resulting in reduced plant growth and potassium leaching. Biochar from woody materials are nutrient poor and need nutrient enhancement prior to soil application. In this study, spruce residues were mixed with spruce/pine ash in different ratios (0-50%) to produce biochar-ash composites at 450°C. The biochar yield (ash-free basis) increased by 80-90% with the addition of 50% ash due to catalytic biochar formation. Consequently, nearly half the amount of wood is needed to produce the same amount of (ash-free) biochar. Mineral release was moderated in the composites compared to pure ash, demonstrated by a lower electric conductivity and % available K content (a factor of 2.5-4.4 lower than in wood ash). Furthermore, the % available chromium content, which is a key potentially toxic element in wood ash, decreased by a factor of 50-160. Soil application of biochar-ash composites decreases the risk of Cr toxicity, salinity stress and leaching of K in soil substantially compared to ash application. Biochar-ash composites are a novel product with vast unexplored potential for use in forestry and agriculture.

Keywords

pyrolysis; potentially toxic element; potassium; heavy metal; forestry; agriculture

Abbreviations

PTE, potentially toxic element; DSC, differential scanning calorimetry; TGA, thermogravimetric analysis; ICP-OES, inductively coupled plasma – optical emission spectrometry

Total Word Count: 8140

1 Introduction

Bioenergy is already the biggest contributor to renewable energy generation in the EU, of which solid biomass combustion makes up the main share (European Commission, 2017). Furthermore, in the Fifth IPCC assessment report, bioenergy generation with carbon dioxide carbon capture and storage (BECCS) is mentioned as a key technology for mitigation of climate change and hence is likely to expand in the near- and mid-term future (IPCC, 2014). Although biomass combustion produces renewable energy, in contrast to e.g. wind or solar power, it also creates ash as a by-product; wood combustion generates around 1% waste ash which is mostly landfilled (Demeyer et al., 2001; Pitman, 2006). Therefore, in light of sustainable resource use and to reduce disposal costs, investigating possible re-use options for wood ash is a very important strategy to increase the sustainability of bioenergy generation.

Due to the high alkalinity of wood ash (pH 8.9-13.5) it can be applied to soil as liming agent to increase the pH (Demeyer et al., 2001; Khanna et al., 1994; Sano et al., 2013). Therefore, it is well suited for reducing the Al and Mn toxicity in acidic forest soils and to increase availability of nutrients already present in soil (Kahl et al., 1996; Nkana et al., 1998). Additionally, in itself it is a good source of nutrients and in particular, it can supply high amounts of available potassium (K) (Demeyer et al., 2001; Pitman, 2006).

The effects of wood ash on soil pH and nutrient status of the soil, however, are only short-lived due to the high solubility of K and Na oxides, hydroxides and carbonates which leach quickly (Ulery et al., 1993). Furthermore, the high K availability, general salinity (high electric conductivity (EC)) and high pH, change the soil chemistry rapidly which can result in toxicity in plants and soil organisms and shifts in soil microbial composition (Augusto et al., 2008; Bang-Andreasen et al., 2017; Demeyer et al., 2001; Etiegni et al., 1991b; Jagodzinski et al., 2018; Qin et al., 2017; Staples and Van Rees, 2001). Therefore, means to create an ash-containing material which supplies nutrients in a more controlled way makes the use of ash in forestry and agriculture much more attractive and therefore, reduces the amount of ash being landfilled and closes the nutrient loops.

Charcoal applied to soil can improve nutrient retention by increasing the cation exchange capacity (CEC) and thus reduce nutrient leaching (Ippolito et al., 2015). The use of charcoal for environmental applications, such as the use in soil, has been extensively studied in the past 10 years and charcoal used for this purpose is generally referred to as biochar (Lehmann and Joseph, 2015). In addition to increases in soil CEC, biochar can have a high water holding capacity, increase soil microbial abundance and have further beneficial effects (Li et al., 2017; Masiello et al., 2015; Thies et al., 2015).

Charred biomass is already present in boreal forest soils in high quantities from forest fires and can comprise up to 40% of the total soil carbon (DeLuca and Aplet, 2008). Therefore, the addition of biochar to soils is not an unnatural intervention and analyses of biochar produced from uncontaminated feedstocks have shown minimal organic contamination (Buss et al., 2016a, 2015; Weidemann et al., 2017). Yet, biochar from woody materials have low nutrient contents (Buss et al., 2016b; Xu et al., 2017) and need nutrient enhancement prior to soil application.

Mixing of wood ash and wood-derived biochar, e.g. made from forest residues, could be a very valuable proposition; the carbon providing general soil improving effects and the ash providing nutrients. Besides direct nutrient provision (Chia et al., 2014), mineral-enriched biochar can improve the plant nutrient use efficiency (Blackwell et al., 2015; Lin et al., 2013). Furthermore, enriched biochars can increase the carbon sequestration potential (lime, clay, ash and manure-enrichment) (Mohammadi et al., 2016), the redox potential (Fe-enrichment) (Pace et al., 2018) and the porosity of biochar (Fe-clay-enrichment) (Rawal et al., 2016).There are two possible ways to produce mineral-enriched biochar; one option is to mix the minerals and biochar after pyrolysis (Blackwell et al., 2015; Chia et al., 2014; Lin et al., 2013); the other option is to mix the minerals with the biomass feedstock before pyrolysis (as e.g. done in Pace et al., 2018 and Rawal et al., 2016).

As wood ash contains high concentrations of K, Na, Ca and Mg (Pitman, 2006), which are known to catalyse biochar formation and increase biochar yield (Eom et al., 2012; Fuentes et al., 2008; Nowakowski et al., 2007), mixing of biomass feedstocks and wood ash prior to pyrolysis could bring additional benefits. However, to our knowledge so far no study has investigated the effects of wood ash-amendment prior to pyrolysis. There is a need to study the effects of wood ash on biochar formation and on the properties of the resulting biochar.

The research question that was addressed in this study was whether biochar-ash composites have superior properties over pure biochar or pure ash application for forestry and agriculture. In this study, spruce forestry residues amended with extra 0%, 5%, 10%, 20% and 50% spruce/pine ash were pyrolysed at 450°C and characterised for agronomically relevant parameters (total/available nutrient and potentially toxic elemental content, pH, EC). Additionally, the influence of wood ash on pyrolysis was investigated via thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

2 Materials and Methods

2.1 Feedstock preparation

A protocol for developing ash-enriched wood pellets was specifically developed for this study. The aim was to blend wood ash and spruce wood residues (*Picea abies*) to create a composite material with high degree of contact between the organic and mineral components (to maximize potential catalytic reactions) that could be pyrolysed in a continuous pyrolysis unit. Pelletizing ensured that the mixture remained homogenous and density separation of the two materials was avoided. Furthermore, pelletizing enables easy storage and handling of the final biochar-ash composites.

The ash originated from a district heating plant in Bureå south of Skellefteå in Sweden, and is owned by Skellefteå Kraft AB. It is a 2MW moving inclined grate (HOTAB) with a Danstoker boiler (steam temperature 140°C, 4.2 bar). A blend of pelletized spruce and pine sawdust was used in the biomass boiler with a mean moisture content of 6.7%, ash content of 0.3%, a bulk density of ~680 kg L^{-1} and a heating value of ~20.3 MJ kg^{-1} dry matter. After combustion, the ash is ejected via a screw to a container in which fly ash and bottom ash were mixed, and where samples were collected.

To fully incorporate the ash into the wood and subsequently into the biochar, the spruce wood was ground to a particle size of < 2 mm using a blender (Philips HR 2810/A) and the wood ash was sieved to < 0.5 mm. Different ash-to-spruce ratios were prepared: 0%, 5%, 10%, 20% and 50% on dry-basis. A customised stainless-steel die with a 1-inch diameter was used to produce pellets with 3 g dry weight. The respective amounts of spruce and wood ash were mixed in polypropylene bags; 2 mL of water was added for better mixing, to avoid density separation and to decrease dust formation. Two pellets were produced at a time in the die, separated by a stainless-steel spacer. The die was closed with a vice to ensure that the same amount of pressure was applied to all pellets of the same treatment. Due to the higher density of wood ash compared to spruce, increasing wood ash concentrations increased the density of the pellets. Hence, to ensure similar pressures, additional spacers were added with increasing wood ash concentration. The extra height of the spacers and the resulting densities of the pellets are shown in SI Table 1.

Afterwards, the die was placed in an oven for stable pellet formation through binding of the materials. Different residence times and oven temperatures were tested to obtain stable pellets, and 160°C for 1.5 h was selected and used for production of 12-16 pellets with 3 g for each of the five treatments.

For biochar yield comparison untreated spruce cylinders with a diameter and height of 15 mm were prepared as well.

2.2 Biochar production

2.2.1 Continuous auger reactor

Feedstock amounts of 36-45 g were pyrolysed in the Stage II, auger reactor, pyrolysis unit of the UK Biochar Research Centre. Details about the unit can be found elsewhere (Buss et al., 2016b). A highest treatment temperature (HTT) of 450°C was chosen to minimize the availability of minerals present in the ash (Buss et al., 2016a). A mean residence time in the heated zone of 450°C of 20 min was used (corresponds to around 10 min at HTT) and a nitrogen carrier gas flow rate of 1.5 L min^{-1}. The biochar yield on dry basis and biochar yield based on dry, ash-free basis (daf) (g daf biochar / g daf feedstock) were calculated (ash contents measured in TGA, see 2.3.1).

2.2.2 Thermogravimetric analysis (TGA) - pyrolysis

Micro-pyrolysis was performed with a Mettler-Toledo TGA/DSC1 to replicate the conditions in the continuous unit (450°C HTT, 10 min RT at HTT, 90°C min^{-1} heating rate) for accurate biochar yield determination. The pellets were cut into smaller pieces and ~40 mg was pyrolysed in 150 µL crucibles. The analysis was performed in triplicates. Differential scanning calorimetry (DSC) curves were automatically derived by the TGA. Mean ± standard deviation of biochar yield on dry basis and biochar yield based on dry, ash-free basis (daf) (g daf biochar / g daf feedstock) were calculated.

2.3 Biochar characterisation

The biochar from the auger reactor (Stage II) was ground up using a mortar and pestle as preparation for the following analysis. To ensure representative sampling, most of the produced biochar was ground-up, mixed thoroughly and sub-samples were taken. The analyses were performed in triplicates if not stated otherwise.

2.3.1 Proximate analysis

A Mettler-Toledo TGA/DSC1 was used to perform proximate analysis (Buss and Mašek, 2014) which distinguished between moisture, volatile matter (VM), fixed carbon (FC) and ash content. It used a temperature of 110°C for moisture determination (in nitrogen), 900°C in a nitrogen atmosphere to determine the volatile matter loss and introduced air at 900°C to oxidize the stable carbon (fixed carbon) and the ash fraction remained.

2.3.2 pH and electric conductivity (EC)

EC and pH were determined as recommended by the International Biochar Initiative (IBI) through biochar extraction with distilled water (Rajkovich et al., 2012). A solid-to-liquid ratio of 1:20 was used and the samples were shaken at 150 rpm on an orbital shaker for 1.5 h.

The samples were analysed with a Hach HQ40d portable meter using a Hach conductivity probe CDC 401 and the gel-filled pH-electrode Hach 51935-00.

2.3.3 Extractions and digestions

To determine the total content of potentially toxic elements (PTEs) and nutrients, modified dry ashing was used to digest the biochars (and feedstocks) which was optimised for use on biochar previously (Enders and Lehmann, 2012). The method combines dry ashing at 500°C (also used for ash content determination, Table 1) with wet digestion using HNO_3 and H_2O_2. The original method was modified in two aspects as previously explained (Buss et al., 2016b) to increase the limit of detection.

The availability of elements in biochar was determined through extraction with 0.01 M $CaCl_2$ which has shown to correlate well with plant uptake for P and K (and B, Mn, Mo and Na) in a study on biochar where typical soil extractants were compared (Shepherd et al., 2017). 1.5 g of biochar was extracted with 15 mL of 0.01 M $CaCl_2$ in 50 mL polypropylene centrifuge tubes. Subsequently, the tubes were shaken on an orbital shaker for 2 h at 150 rpm and were filtered with Whatman No. 1 filter paper. Three blanks with only 0.01 M $CaCl_2$ were included in the procedure.

The digests/extracts were analysed via Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) as described below. In addition, the % available of the total elemental content and the propagated error using the mean (AV) and standard deviation (SD) of the total (n = 3) and the $CaCl_2$-extractable concentrations (n = 3) were calculated.

2.3.4 Elemental analysis

The samples were filtered with Whatman No. 1 filters and analysed via ICP-OES (Varian Vista Pro). Calibration from 0.01 ppm to 25 ppm were used and if outside the detection range, the samples were diluted. The 1 ppm standard was added as quality control after every 15 samples. More details on the ICP analysis data processing can be found elsewhere (Buss et al., 2016b).

2.4 Data processing and statistics

A regression line was fitted to the data from EC measurements (dependent parameter) and either the ash addition prior to pyrolysis or the actual ash content in the biochar (independent parameter) using Sigma plot (Version 13.0, Systat Software Inc.).

3 Results and Discussion

3.1 Biochar production

The biochar yield (dry basis) of ash-amended and pelletized spruce wood increased with the percentage of spruce/pine ash addition from 25.6% (no ash addition) to 65.8% (50% ash addition) (Table 1). This is expected due to the addition of minerals in the form of wood ash which mostly remain in the pyrolysis solids and hence increase the char yield. However, the biochar yield based on the amount of dry, ash-free (daf) biochar and feedstock also increased with wood ash addition. The maximum daf biochar yield was observed at the highest wood ash addition (50%) with a relative increase in biochar yield of 78.1% compared to pyrolysis of pure spruce pellets (Table 1, Figure 1). To our knowledge we report for the first time that external wood ash addition can increase the daf biochar yield.

The daf biochar yield of the treatment amended with 20% wood ash was lower than expected (27.9% daf) compared with the biochar yields from the other treatments pyrolysed in the auger reactor (Table 1, Figure 1). The pellets of the 20% (and 50%) treatment were brittle after pyrolysis and although all twelve pellets could be recovered from the continuous pyrolysis unit, most likely small pieces broke off which affected the biochar yield. Therefore, for accurate yield determination, to confirm the results and to investigate the underlying mechanism the samples were also pyrolysed in a TGA in triplicates.

In the TGA, the daf biochar yields were slightly lower than in the auger reactor (Table 1), probably due to reduced secondary biochar formation resulting from reduced particle size and a lower residence time of vapours trapped within the particles (Antal and Grønli, 2003). But generally, the yields were in a similar range confirming the yield increases caused by wood ash addition as observed in the auger reactor (Figure 1). In the TGA 50% ash addition resulted in a daf biochar yield increase of 89.8% ± 17.4 (Figure 1, SI Table 2).

The DSC curves derived from pyrolysis at 450°C in the TGA clearly show a reduction of the endothermic peak with wood ash addition (Figure 2) as also described when biomass was impregnated with individual minerals, such as potassium acetate (Fuentes et al., 2008). The 10% ash treatment resulted in the highest exothermic peak which decreased with higher ash addition and 50% ash-amended spruce showed the lowest energy flow per mg of material. It is also apparent that the exothermic peak shifts to a lower temperature with a higher addition of wood ash. The catalytic effects of individual minerals during pyrolysis are well established in the literature (Eom et al., 2012; Fuentes et al., 2008; Nowakowski et al., 2007) but here we were able to demonstrate that wood ash can have the same effect. This is based on catalytic processes which lower the activation energy needed for reactions to take place.

To our knowledge, we documented for the first-time biochar yield increases as a result of the amendment of woody biomass with wood ash. A key step was the pelletizing which ensured a homogenous distribution of the externally added ash in the pellets and allowed efficient reactions between the mineral and organic phase. Consequently, catalysis effects between wood ash and biomass (spruce) took place which boosted the biochar yield. As a result, wood ash addition improved the conversion efficiency of spruce to biochar significantly; 80-90% less spruce was needed to yield the same amount of (ash-free) biochar, and thus brings major economic and environmental advantages.

3.2 Key biochar properties related to soil amendment use

3.2.1 Electric conductivity (EC) and pH

Spruce/pine ash addition elevated the EC of our biochars substantially (Table 1). In soil, the EC increases linearly with the dose of wood ash application (Bang-Andreasen et al., 2017). In contrast, Figure 3 shows an exponential increase of EC with ash content in the five biochars and the wood ash sample. Pure wood ash had an EC of 13250±380 µS cm^{-1}, 4.8 times and 11.2 higher than the EC in the biochar sample amended with 50% and 20% ash, respectively, highlighting biochar's immense sorption capacity. While pure ash releases most of its minerals immediately, biochar can buffer this release and hence reduce the EC of the biochar-ash composites drastically. This is an important finding for the application of biochar-ash composites.

Increasing contents of wood ash in biochar also increased the pH of the composite. Pure wood ash was highly alkaline with a pH of 12.75 (Table 1), comparable to the pH of ashes reported elsewhere (Someshwar, 1996). The pH of the biochar amended with 50% wood ash prior to pyrolysis was 0.7 pH units lower. A direct comparison of the pH values as done for the EC in Figure 3 is not possible because the pH scale is a logarithmic scale, but these results clearly show that biochar can buffer the EC and pH effects of wood ash.

Increasing soil pH is important for forest soils as they are predominantly acidic. However, due to the rapid changes in soil pH and soil EC imposed by wood ash (Ulery et al., 1993; Williams et al., 1996), over application, which results in phytotoxicity (Etiegni et al., 1991b; Jagodzinski et al., 2018; Staples and Van Rees, 2001) and shifts in microbial composition (Bang-Andreasen et al., 2017) happens readily. Therefore, the ability of biochar to buffer the release of minerals from ash, and associated soil pH and EC effects, is invaluable in creating a safe and more effective biochar-ash product that can still increase the pH but in a more controlled way and over a longer period of time. In follow-up studies the liming performance of biochar-ash composites should be directly compared with pure wood ash and lime.

3.2.2 Nutrients

The wood ash sample contained around 25% Ca, 4% K, 5% Mg, 3% Mn and 1.4% P (Table 2) which is similar to wood ash reported elsewhere (Etiegni et al., 1991a). Due to the comparatively low temperature treatment (450°C), nutrients did not evaporate during pyrolysis and the total nutrient concentrations in the ash-amended biochars were proportional to their wood ash additions.

Magnesium (Mg) and manganese (Mn) were largely unavailable (Table 2, SI Table 3), as previously reported for various combustion wood ashes in Sano et al. (Sano et al., 2013). The calcium (Ca) availability was not measured in our study as the extraction was performed with $CaCl_2$. Other studies reported low Ca availability in combustion ashes (Nieminen et al., 2005).

The availability of phosphorus (P) was very low in both, wood ash and biochar, below the limit of detection in most cases (0.26 mg kg^{-1}) (Table 2). Phosphorus in wood ash and biochar is bound predominantly in unavailable forms, e.g. in calcium phosphates (Liang et al., 2017; Sano et al., 2013; Steenari et al., 1999; Uchimiya and Hiradate, 2014). However, in Erich and Ohno, the plant stimulating effect of wood ash could be attributed to increases in plant P supply (Erich and Ohno, 1992). In addition, elevating the soil pH of acidic soils can increase the availability of P already present in soil; the ideal soil pH for maximum P availability is 6.0-6.5 (Blume et al., 2016) and therefore addition of alkaline biochar (such as the biochar-ash composite) can have an indirect positive effect on plant P supply. Overall, the potential supply of P in biochar-ash composites to plants needs more investigation.

Potassium (K), was highly available in wood ash, 59.8 ± 4.3% of the total content was available which is similar to Khanna et al. (Khanna et al., 1994) where 68% of K was water-extractable and Sano et al. (Sano et al., 2013) where 78.5-103.8% of K was water-extractable. Incorporation of wood ash into spruce wood and subsequent pelletizing and pyrolysis at 450°C reduced the percentage of available K to ~14% in the 5%, 10% and 20% ash-amended treatments which is a reduction by a factor of 4.1-4.4 (Figure 4, SI Table 3). The K availability increased in the 50% ash amendment to 24% which is still less than half of the availability in the pure ash treatment. The biochar surfaces capable of retaining nutrients were most likely saturated and hence the K availability increased in the 50% ash-amended biochars compared to the 20% amended ones.

Many studies concluded that no long-term K fertilization effects can be expected when pure wood ash is applied to soils (Kahl et al., 1996; Sano et al., 2013; Ulery et al., 1993; Williams et al., 1996) and even phytotoxic effects are possible due to the high K availability (Etiegni et al., 1991b). With the use of wood ash in biochar, instead of instant leaching of K, we can expect a more moderate supply of K initially and medium to long-term effects. This is a significant and novel finding that makes the use of biochar-ash much more attractive for fertilization than the use of pure wood ash.

3.2.3 Potentially toxic elements (PTEs)

Pure wood ash exceeded several threshold values for total PTEs for biochar and other soil amendments, while the unpyrolysed spruce wood did not exceed any of the threshold values (Table 3, SI Table 4). Cadmium (Cd) and chromium (Cr) are of particular concern as, e.g. the premium biochar threshold limit values for application of biochar to soil (EBC, 2012) were exceeded 4-fold and 7-fold by the ash, respectively. The concentrations of Cu, Ni and Zn in wood ash were just above limit values as well. Such PTE values are not atypical. Compared to average PTE concentrations in 26 wood ashes: As 23.2 mg kg^{-1}, Cd 5.0 mg kg^{-1}, Cr 39.0

mg kg^{-1}, Cu 75.3 mg kg^{-1}, Mo 14.0 mg kg^{-1}, Ni 23.5 mg kg^{-1} and Zn 443 mg kg^{-1} (Someshwar, 1996), in our study only the Cr content in wood ash was slightly higher, but still well within range reported in other studies (16-810 mg kg^{-1}) (Pohlandt-Schwandt, 1999). The origin of Cr can be both, contamination of the feedstock, but also the furnace steel (Buss et al., 2016b; Sano et al., 2013). As expected, the 50% ash-amended biochar exceeded the Cd and Cr threshold values and some of the threshold values for Cu and Ni (Table 3). The 20% ash treatment was just above the total Cd concentration and was still 3-fold higher than the limit for Cr in premium biochar (EBC, 2012).

In the German Federal Soil Protection Ordinance, five threshold values for available PTEs, based on a salt extraction (1 M NH_4NO_3) similar to the one applied in our study (0.01 M $CaCl_2$) have been reported for protection of plant growth and crop quality. None of the threshold values were exceeded by our wood ash and biochars (Table 3) (apart from Zn by pure spruce wood). This clearly demonstrates the ability of ash and biochars to sorb PTEs strongly and efficiently.

In the German Ordinance, no threshold value exists for Cr and the percentage available (0.01 M $CaCl_2$-extractable) of the total elemental content in wood ash was high for Cr with 8% (Figure 4, SI Table 5). Cr is released readily from wood ash (Demeyer et al., 2001) and therefore, high Cr availability is a frequent problem in combustion ash, in particular Cr (VI) which is the oxidation state that demonstrates higher stability and availability in alkaline environments such as wood ash provides (Kabata-Pendias, 2011; Pohlandt-Schwandt, 1999; Sano et al., 2013). While Cr (III) is essential for animals and humans, Cr (VI) is toxic to plants, animals and humans (Kabata-Pendias, 2011; Pohlandt-Schwandt, 1999). Therefore, Cr possess a high risk to soils when wood ash is used in agriculture or even when landfilled (Pohlandt-Schwandt, 1999).

The incorporation of wood ash into spruce and conversion into biochar reduced the availability of Cr drastically from 8.00 ± 0.25% (pure ash) to 0.05 ± 0.00% (20% ash biochar) - 0.15 ± 0.01% (5% ash biochar) which is a reduction by a factor of 54-160 (Figure 4, SI Table 5). Substantially reduced Cr availability in different types of biomass after pyrolysis was also observed in other studies (Buss et al., 2016a; Farrell et al., 2013). However, here we showed that even externally added Cr in the form of wood ash which is not already incorporated into the plant structure is efficiently immobilised. This mitigates a typical problem of wood ash for soil application, high Cr availability.

3.3 Environmental and agronomic benefits of biochar-ash composites

In this study, we demonstrated that the production and application of wood-ash-enhanced biochar to soil has multiple benefits over pure biochar or pure wood ash application.

Wood ash application can result in significant changes in soil solution chemistry as the soil exchange sites are not able to buffer the high load of cations. However, blending of wood ash with wood, pelletizing and subsequent conversion into biochar effectively moderates the release of cations and reduces the EC and available K significantly compared to pure wood ash. Therefore, adverse effects in soil due to high salinity are less likely. Indeed, post-production mixing of biochar and ash and application to plants reduced ash-related phytotoxicity (Saletnik et al., 2016). Although this is different from the application of composite materials as proposed in our study, the use of composites is likely to be even more effective due to the close contact of biochar and ash. Furthermore, our results show reduced availability and leaching of K which should result in a higher plant K use efficiency. The availability of Cr, a key contaminant in wood ashes, is drastically reduced in biochar-ash composites, minimising the risk for adverse plant effects. These are significant new findings.

Generally, biochar can improve the cation exchange capacity, water holding capacity and structure of the soil, both, in the short and long-term (Glaser et al., 2002; Lehmann and Joseph, 2015; Li et al., 2017) and pelletised biochar showed to be particularly beneficial. Pelletised biochar applied in 14 t ha^{-1} increased the plant available water content and water retention in soil (Andrenelli et al., 2016). Pellets made from biochar and wood flour applied to growing media in 25% also increased the plant water availability (Dumroese et al., 2011). Moreover, pelletising of biochar reduced the release of fine particles, and hence increased the carbon sequestration potential of biochar and decreased the health risk due to dust formation during biochar application (Maienza et al., 2017). We expect that our biochar-ash composite has similar effects, which will be the focus of follow-up studies. Overall, the incorporation of ash into pelletised biochar-ash composites makes it a superior product compared to application of pure ash as it also adds a (stable) carbon fraction (biochar).

There are also multiple benefits of using biochar-ash composites over the production and use of biochar from pure woody biomass. First, the biochar yield increases and therefore, less biomass is needed to produce the same amount of biochar. This has economic and environmental benefits; less CO_2 is released, and more carbon is available to be sequestered in the ground as biochar. Secondly, the biochar is nutrient loaded, with K, Ca, Mg and P.

In practise, uncontaminated ash from biomass boilers and parts of the unburned wood (or saw dust from timber industry or forestry residues) can be mixed and pelletized with existing pelletizing equipment. Subsequently, the pellets can be pyrolysed at relatively low temperatures (450-500°C) to create a nutrient-rich biochar with high surface functionality (decreasing surface functionality with higher pyrolysis temperatures (Gai et al., 2014)). The biochar-ash pellets can be easily spread on forest (or agricultural) soils with on-site conversion and minimal transportation, closing the nutrient loop.

Wood ash provides the nutrients, such as K, Mg, Ca, P and micronutrients, while the organic part of the biochar buffers and moderates the nutrient release, hence, increases the nutrient use efficiency and brings further soil benefits (Li et al., 2017). In addition, charging this biochar-ash composite with sources of available N could create a highly functional product for improvement of soil properties and fertilization. The use of the biochar-ash composites as fertilizer brings an immediate financial incentive and improves environmental sustainability, while long-term positive effects are expected from soil improvements of biochar.

4 Conclusion

Expansion in the bioenergy sector makes it necessary to find a use for nutrient-rich wood ash that can potentially cause detrimental soil effects. Here we present a strategy to address this problem: mixing of wood ash with woody forestry residues and pyrolysis at relatively low temperature. This results in a product which will change the soil solution less rapidly than wood ash but for a longer time. It provides nutrients and changes the pH in a more controlled way and demonstrates a significantly reduced available Cr concentration. This study clearly demonstrates that biochar-ash composites are very promising as organo-mineral fertilizers, opening a new field of research and applications for biomass ash in a circular economy.

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Table 1: Proximate analysis, biochar yields, pH and electric conductivity (EC) of feedstock and biochar produced in the auger reactor. Mean and one standard deviation for the proximate analysis (n = 3) are reported and single values for the biochar yield. The ash content was determined at 500°C and 900°C in air. PSC, pyrolysed spruce cylinders; PPS, pelletised and pyrolysed spruce; NA, not applicable; % change, % change compared to the unamended biochar (PPS 0% 450°C).

	ash 500°C	ash 900°C	volatile matter	fixed carbon	char yield			pH	EC
	% dry	% dry	% daf	% daf	% dry	% daf biochar/ daf feed	% change		$\mu S\ cm^{-1}$
wood ash	93.6 ± 0.3	84.4 ± 0.7	80.6 ± 3.7	19.4 ± 3.7	NA	NA	NA	12.75 ± 0.04	13250 ± 380
spruce	0.2 ± 0.2	0.9 ± 0.2	83.3 ± 0.5	16.7 ± 0.5	NA	NA	NA	10.09 ± 0.06	37.8 ± 10.7
PSC 0% 450°C	0.6 ± 0.2	3.1 ± 0.5	23.9 ± 0.3	76.1 ± 0.3	25.6	25.0	NA	8.78 ± 0.30	59.8 ± 12.9
PPS 0% 450°C	0.7 ± 0.4	2.0 ± 0.3	20.0 ± 0.6	80.0 ± 0.6	24.0	23.7	0.0	8.86 ± 0.05	53.0 ± 1.1
PPS 5% 450°C	16.5 ± 0.5	17.2 ± 0.7	22.3 ± 0.1	77.7 ± 0.1	31.4	27.5	16.1	10.43 ± 0.07	276 ± 1
PPS 10% 450°C	25.9 ± 1.4	23.1 ± 2.3	24.0 ± 0.5	76.0 ± 0.5	35.3	29.5	24.7	10.63 ± 0.04	444 ± 9
PPS 20% 450°C	42.7 ± 3.3	42.9 ± 0.9	32.5 ± 0.0	67.5 ± 0.0	40.4	27.9	17.9	11.60 ± 0.08	1185 ± 15
PPS 50% 450°C	68.7 ± 1.0	62.1 ± 0.7	47.8 ± 0.5	52.2 ± 0.5	65.8	42.1	78.1	12.07 ± 0.03	2765 ± 21

Table 2: Total and 0.01 M $CaCl_2$-extractable concentrations of nutrients in biochars and feedstocks as mean and one SD (n = 3). Only total concentration of Ca determined. PSC, pyrolysed spruce cylinders; PPS, pelletised and pyrolysed spruce.

		K	Mg	Mn	B	P	Ca
available							
wood ash	mg kg^{-1}	23200±1660	< 2.3	< 0.009	< 3.2	< 0.26	
spruce	mg kg^{-1}	154±22	77.7±8.05	51.9±4.92	< 3.2	1.72 ± 1.17	
PSC 0% 450°C	mg kg^{-1}	172±20	35.5±5.72	3.04±0.26	< 3.2	1.36 ± 0.23	
PPS 0% 450°C	mg kg^{-1}	170±12	4.52±0.89	2.83±0.24	< 3.2	1.11 ± 0.30	
PPS 5% 450°C	mg kg^{-1}	665±19	116±5.56	0.60±0.06	< 3.2	0.34 ± 0.15	
PPS 10% 450°C	mg kg^{-1}	1070±61	102±3.64	< 0.009	< 3.2	< 0.26	
PPS 20% 450°C	mg kg^{-1}	2090±22	80.6±1.25	1.08±0.08	< 3.2	< 0.26	
PPS 50% 450°C	mg kg^{-1}	5170±127	< 2.3	0.26±0.16	< 3.2	< 0.26	
total							
wood ash	mg kg^{-1}	38900±553	53600±998	32700±751	248±5.79	13700 ± 230	254000 ± 5150
spruce	mg kg^{-1}	85.8±21.9	68.7±31.7	43.2±20.9	< 71.8	13.2 ± 6.51	390 ± 169
PSC 0% 450°C	mg kg^{-1}	541±186	162±105	145±71.5	< 71.8	< 10.3	1490 ± 716
PPS 0% 450°C	mg kg^{-1}	670±115	177±84.9	186±70.4	< 71.8	15.2 ± 7	1850 ± 631
PPS 5% 450°C	mg kg^{-1}	4749±210	8690±448	5520±283	33.5±2.28	1980 ± 112	43000 ± 2170
PPS 10% 450°C	mg kg^{-1}	7876±221	13600±794	8790±400	60.1±3.21	3000 ± 132	68600 ± 3260
PPS 20% 450°C	mg kg^{-1}	14400±646	23000±2890	12500±1660	127±13.8	5080 ± 513	129000 ± 16200
PPS 50% 450°C	mg kg^{-1}	21600±1150	36600±774	20100±333	223±3.16	11400 ± 213	206000 ± 4090

Table 3: Total and 0.01 M $CaCl_2$-extractable concentrations of PTEs in biochars and feedstocks as mean and one standard deviation (n = 3). As comparison, the following threshold values are from the German Federal Soil Protection Ordinance for protection of plant growth and crop quality based on NH_4NO_3-extractions: As 0.4 mg kg^{-1}, Cd 0.1 mg kg^{-1}, Cu 1 mg kg^{-1}, Ni 1.5 mg kg^{-1}, Pb 0.1 mg kg^{-1}, Zn 2 mg kg^{-1} (German Federal Soil Protection and Contaminated Sites Ordinance, 1999). PSC, pyrolysed spruce cylinders; PPS, pelletised and pyrolysed spruce.

		As	**Cd**	**Co**	**Cr**	**Cu**	**Hg**	**Mo**	**Ni**	**Pb**	**Zn**
available											
wood ash	mg kg^{-1}	< 0.13	< 0.12	< 0.01	42.9±1.25	< 0.004	< 0.87	2.83±0.08	0.05±0.01	< 0.12	0.60±0.05
spruce	mg kg^{-1}	< 0.13	< 0.12	0.01±0.002	0.01±0.00	0.05±0.02	< 0.87	< 0.46	0.03±0.01	< 0.12	4.28±0.25
PSC 0% 450°C	mg kg^{-1}	< 0.13	< 0.12	< 0.01	< 0.002	0.02±0.01	< 0.87	< 0.46	< 0.009	< 0.12	0.13±0.03
PPS 0% 450°C	mg kg^{-1}	< 0.13	< 0.12	< 0.01	< 0.002	< 0.004	< 0.87	< 0.46	0.05±0.01	< 0.12	0.53±0.10
PPS 5% 450°C	mg kg^{-1}	< 0.13	< 0.12	< 0.01	0.14±0.00	< 0.004	< 0.87	< 0.46	< 0.009	< 0.12	< 0.01
PPS 10% 450°C	mg kg^{-1}	< 0.13	< 0.12	< 0.01	0.19±0.00	< 0.004	< 0.87	< 0.46	< 0.009	< 0.12	< 0.01
PPS 20% 450°C	mg kg^{-1}	< 0.13	< 0.12	< 0.01	0.11±0.00	0.02±0.00	< 0.87	< 0.46	< 0.009	< 0.12	< 0.01
PPS 50% 450°C	mg kg^{-1}	< 0.13	< 0.12	< 0.01	0.20±0.01	0.11±0.02	< 0.87	< 0.46	< 0.009	< 0.12	< 0.01
total											
wood ash	mg kg^{-1}	5.77±0.32	4.04±0.07	11.3±1.25	537±6.38	142±2.72	< 30.6	32.7±0.07	49.0±0.11	33.5±0.54	373±5.78
spruce	mg kg^{-1}	< 1.20	0.02±0.02	< 0.21	0.76±0.18	1.11±0.40	< 30.6	< 11.2	< 0.10	< 1.41	4.21±1.56
PSC 0% 450°C	mg kg^{-1}	< 1.20	0.02±0.02	< 0.21	< 0.13	2.94±0.75	< 30.6	< 11.2	0.38±0.08	0.63±0.44	17.6±7.81
PPS 0% 450°C	mg kg^{-1}	< 1.20	0.07±0.03	< 0.21	2.54±0.85	36.9±11.1	< 30.6	< 11.2	5.65±2.49	3.17±0.33	40.5±40.8
PPS 5% 450°C	mg kg^{-1}	< 1.20	0.31±0.02	2.31±0.12	91.9±5.48	33.0±4.41	< 30.6	< 11.2	14.9±2.36	6.60±0.67	101±5.20
PPS 10% 450°C	mg kg^{-1}	< 1.20	0.39±0.04	3.26±0.14	142±6.94	42.2±0.76	< 30.6	< 11.2	22.1±0.39	9.06±0.23	141±2.25
PPS 20% 450°C	mg kg^{-1}	2.94±0.79	1.75±0.21	4.59±0.23	226±16.6	69.9±6.23	< 30.6	< 11.2	26.8±2.16	9.80±0.33	192±13.1
PPS 50% 450°C	mg kg^{-1}	3.70±0.37	3.22±0.09	6.52±0.15	352±8.82	107±0.56	< 30.6	< 11.2	38.8±1.00	17.8±0.47	275±4.27

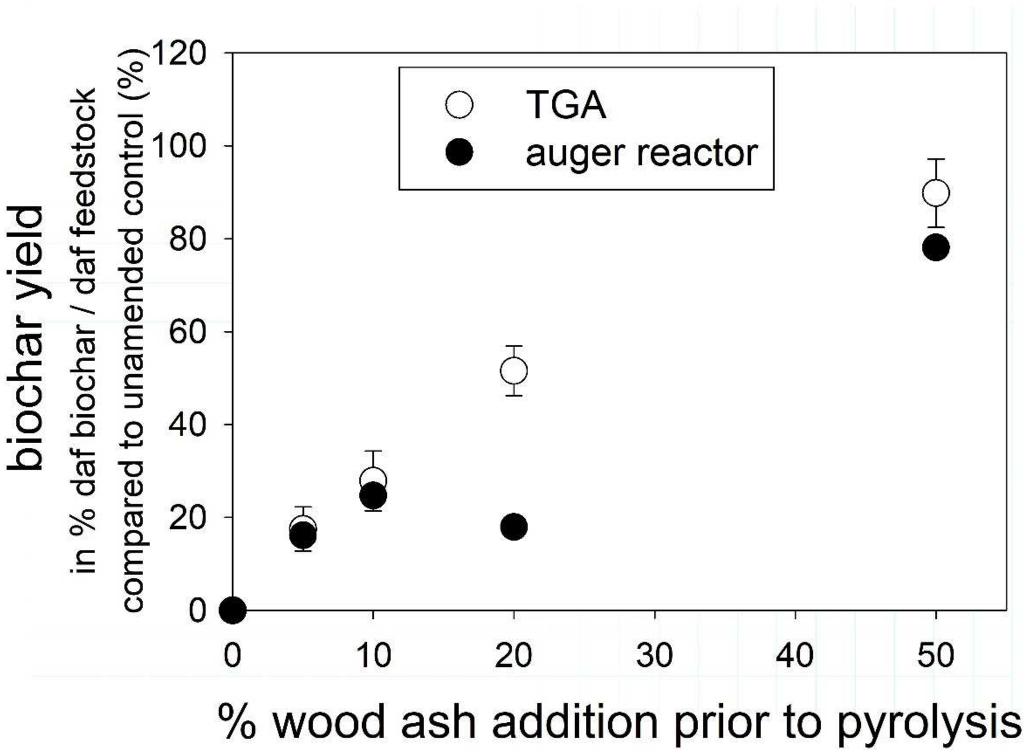

Figure 1: Effect of wood ash addition on biochar yield (in % dry, ash-free biochar / dry, ash-free feedstock) compared to the unamended control in % performed in a TGA (n = 3) and the auger reactor (n = 1). No standard deviation shown here for auger reactor, raw values can be found in Table 1 and SI Table 2.

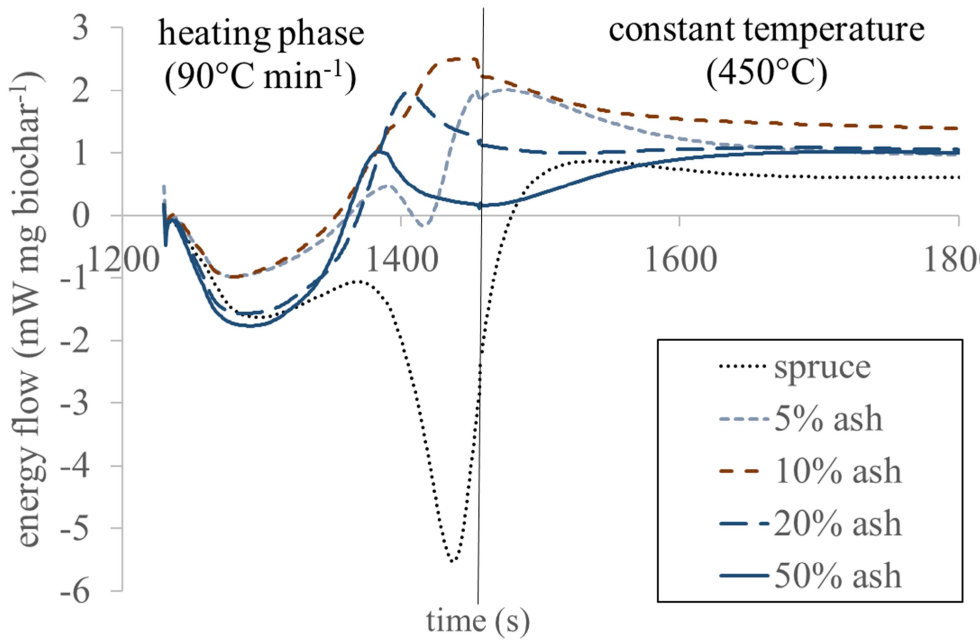

Figure 2: DSC curve from pyrolysis of spruce in a TGA at 450°C with different percentages of wood ash additions. Initial stages of moisture removal at 110°C not shown, starting with heating phase at 90°C min^{-1} heating, followed by an isothermal phase at 450°C for ~10 min.

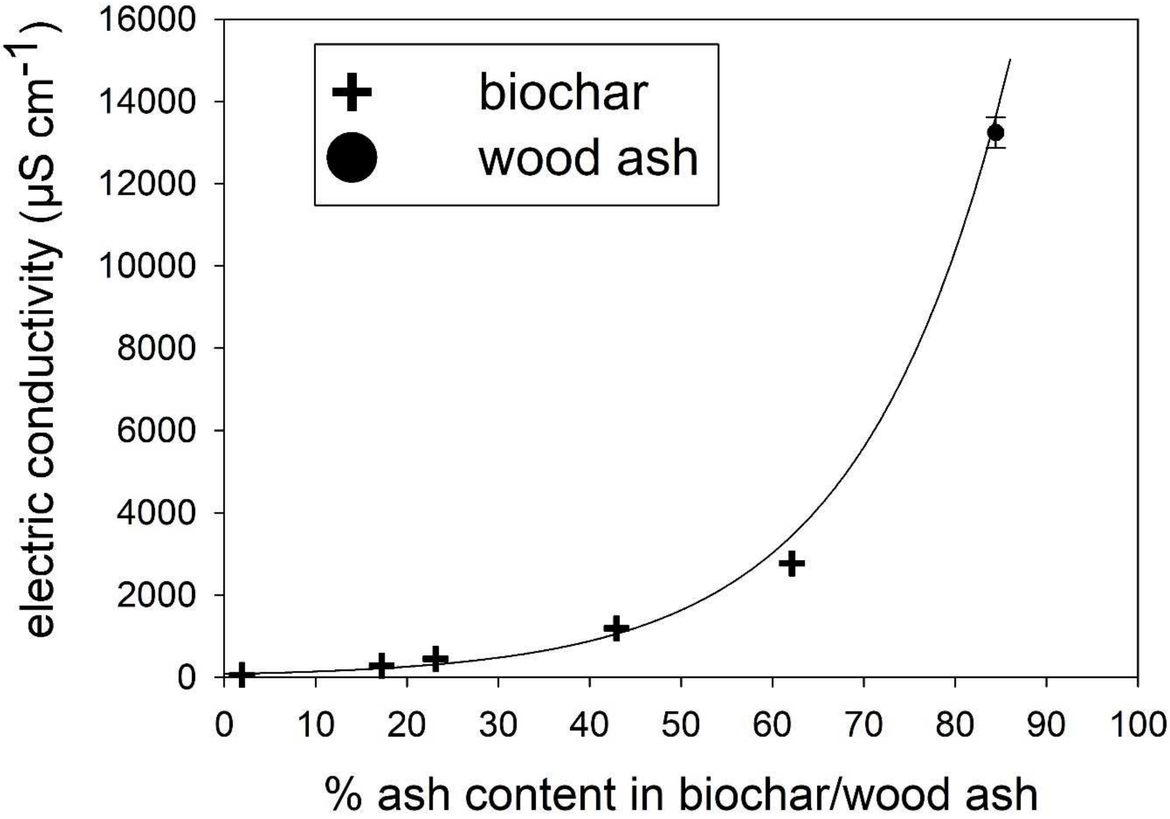

Figure 3: Relationship between electric conductivity (EC) in biochar/pure wood ash with ash content in the materials. Ash contents determined via TGA through combustion in air at 900°C (wood ash with ~16% residual carbon). An exponential curve of type y = a * e^{bx} was fitted to the data. Mean EC values with standard deviation of duplicate analyses are shown.

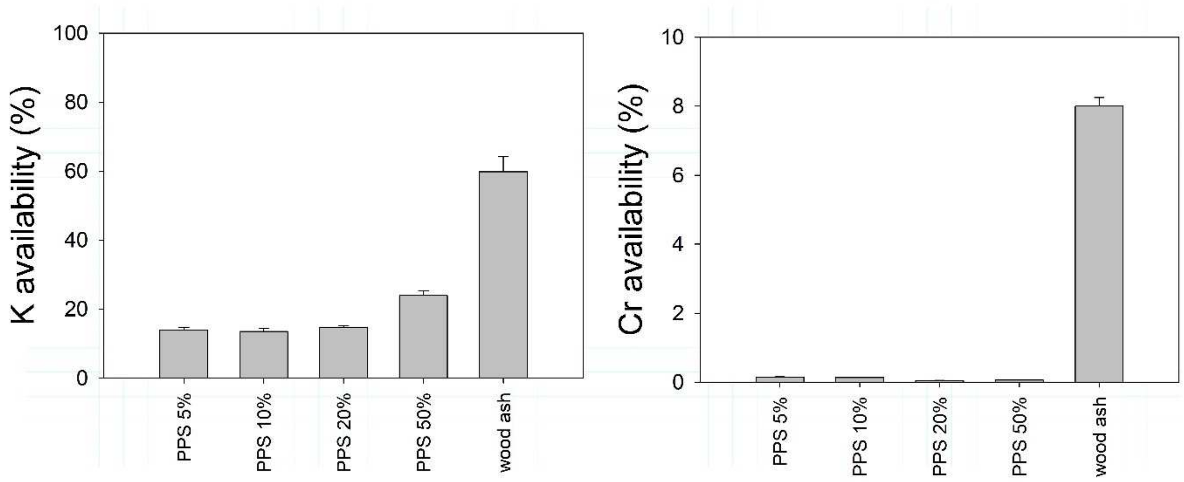

Figure 4: Elemental availability of K and Cr as % 0.01 M $CaCl_2$ extractable of the total elemental content in 450°C biochar with varying ash contents (%) and in pure wood ash. PPS, pelletised and pyrolysed spruce 450°C.

Highlights

- Wood ash was mixed with pine wood and pyrolysed to create biochar-ash composites
- Biochar yield on ash-free basis was increased by 80-90% with 50% wood ash addition
- The percentage available of the total Cr content decreased by a factor of 50-160
- The EC and available K content of the biochar was also significantly reduced
- Biochar-ash composites are very promising organo-mineral fertilisers